Title:
The Application of Polymer Processing Additives (PPAs) for Polypropylene Film: Processing Benefits without Affecting Printing, Sealing and Other Surface Properties

Intro:
Fluoropolymer based polymer processing additives (PPAs) are widely used in polyethylene (PE) for such benefits as melt fracture elimination, productivity improvements, die build-up elimination and gel reduction. The use of these materials in other polyolefins, such as polypropylene (PP), has been limited due to significant differences in rheological behavior of PP vs. PE, and PPA product technology. These limitations have recently been surpassed with new PPA technology.

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The Application of Polymer Processing Additives (PPAs) for Polypropylene Film: Processing Benefits without Affecting Printing, Sealing and Other Surface Properties

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INTRODUCTION

Fluoropolymer based polymer processing additives (PPAs) are widely used in polyethylene (PE) for such benefits as melt fracture elimination, productivity improvements, die build-up elimination and gel reduction\textsuperscript{1-5}. The use of these materials in other polyolefins, such as polypropylene (PP), has been limited due to significant differences in rheological behavior of PP vs. PE, and PPA product technology. These limitations have recently been surpassed with new PPA technology\textsuperscript{6}.

Significant benefits have been realized with the use of Dynamar™ FX 5911X in polypropylene film, pipe, fiber and other extrusion processes. For polypropylene film, benefits include reduced die lip build-up, improved molecular weight (MFR) stability, better gauge control, reduced gel formation and faster color transitions. All of these benefits can increase converter productivity by improving product quality and reducing equipment downtime. Examples of PP film benefits are presented for commercial applications and are based on commercial PP formulations.

But do these benefits come with a cost in terms of surface and mechanical properties? Data in this paper show that Dynamar FX 5911X does not reside in sufficient quantities on the surface to affect the printing, sealing, coating, slip and mechanical properties of PP film (and inferentially for other extruded articles). Understanding the PPA mechanism can reveal how it provides benefits at the polymer/extruder interface but does not affect the surface of the extruded article.

Though the PPA is designed to go to the polymer melt/extruder interface, it is only mobile in the melt. The molecular weight of the fluoropolymer is too high to allow it to bloom to the surface after extrusion. In fact, the fluoropolymer can be seen as discrete droplets in the polypropylene matrix (Photos 1 & 2). The size of these droplets indicates the degree of dispersion of the PPA and good dispersion will yield a better PPA performance. Over a period of time a thin coating of fluoropolymer is formed on the die. The drop in die pressure, to a new steady state, indicates the coating (or “conditioning”) time. The PPA coating is in a dynamic equilibrium. This implies that the level at the surface is at or below the level in the bulk of the host polymer, generally 100 -1000 ppm. Essentially there is too low a concentration of fluoropolymer near the surface of the extruded article to change the surface properties of the host resin.

Similar work has been published to address these types of concerns for Dynamar PPAs in linear low density polyethylene (LLDPE) and polyolefin plastomers (POP) \textsuperscript{7,8}.

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{photo1}
\caption{Photo 1}
\end{figure}

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{photo2}
\caption{Photo 2}
\end{figure}

\textbf{Fluoropolymer is immiscible in the polypropylene matrix. The size of the droplet can also indicate the level of dispersion. These are two different masterbatches of 3\% Dynamar FX 5911X PPA in a 5 MFR polypropylene carrier resin with different processing conditions revealing a better dispersion for the top sample. Photo 1 is 2.5 times the magnification of Photo 2 (250X vs. 100X).}
Experimental

Materials
Polypropylene: 2.5 MFR homopolymer
Processing Aid: Dynamar™ Polymer Processing Additive FX 5911X
Filler/Pigment: 70% CaCO₃ Masterbatch
Pigment: 70% TiO₂ Masterbatch

Film Samples for Printability and Surface Properties
Bi-axially oriented polypropylene (BOPP) films were made on a Bruekner cast film extruder coupled to a 0.18m (7") die with a die gap of approximately 1.0 mm (40 mils). Melt temperature was approximately 230°C (450°F). Output rate for the line was 20.4 kg/hr for a shear rate of approximately 250 s⁻¹. Both the control and the PPA containing samples were extruded for 48 hours. At approximately the 40-hour point, a roll of material was collected for surface and physical property measurements. Films were tentered and stretched 5X in the machine direction (MD) and 9X in the transverse direction (TD).

Film Samples for Physical Property Measurements
Natural and white (containing 10% CaCO₃ from 70% CaCO₃ concentrate) BOPP films were made on the same Bruekner line with the same setup as the films made for surface property analysis. Melt temperature was approximately 230°C (450°F).

Die Build-up Experiments
Die build-up work was done on an Instron Capillary Rheometer with the same PP base resin containing 3% TiO₂ from concentrate. The die was 0.508 mm in diameter and had a 40/1 Length/Diameter (L/D). The apparatus was controlled to a temperature of 230°C (450°F). A single barrel was extruded, the die removed and the die build-up recorded by photograph from a reflective light microscope at 20X magnification.

Corona Treatment
Corona treatment was performed using two ceramic electrodes with a bare-metal chrome roll as the back-up roll. The electrode gap was 1.8 mm. The films were treated using a corona energy of 0.2 J/cm² with a film speed of 80 µm. The films were maintained at 20°C (68°F) during the treatment. The humidity during the treatment was 28%. Following the corona treatment, both films had ASTM wetting test values of approximately 37 dyne/cm.

Electron Spectroscopy for Chemical Analysis (ESCA)
Samples of the PP film after extrusion, after corona treatment and after corona treatment and aging were analyzed by ESCA for fluorine, carbon, silicon and oxygen content on the surface.

Samples were exposed to an X-ray under high vacuum, which interrogates the first 20 to 100 Angstrom depth into the surface. These high-energy photons cause atoms to emit electrons, by the Einstein effect, with a quantum of energy specific to the element. These emitted electrons are detected at 3 different angles of take-off, which allows one to determine the elemental composition as a function of depth into the surface. Higher take-off angles correspond to deeper interrogation depths.

Static Secondary Ion Mass Spectroscopy (SSIMS)
Samples of PP films were bombarded with a high energy (3.5kV), low current (1.5nA) Xenon (Xe⁺) ion beam in a high vacuum. The beam is kept low so that the sample is kept under “static” conditions (minimal surface damage or change). At the same time the sample is bombarded with an electron beam that removes and ionizes the surface. Of the material removed from the surface, about 5% is ionized. The ions are accelerated by a series of lenses through a sector analyzer and through a quadrupole mass spectrometer. The ion mass/charge ratio is measured as well as the ion current at that mass charge ratio. The resolution is set at 0.25 atomic mass units (AMU). This technique is not quantitative, but the fragmentation is very reproducible. These fragments can be used as a means of identification (comparing to a library of spectra) or as a means of comparing two differently prepared samples (as in this case).

Contact Angle
Measurements of the advancing and receding contact angles, of deionized, filtered water were made using the Wilhelmy plate method on a Cahn DCA-322 dynamic contact-angle instrument. The surface tension of the water was measured on each day that samples were analyzed. A three-layer laminate was prepared using Scotch™ 666 double-coated tape to mount the treated sides of the films outward. To prevent contamination during the preparation of this laminate, the treated surfaces were only contacted with untreated polypropylene film. This situation is analogous to the common practice of winding modified film into roll form after treatment. The laminate was cut into a 2.54 x 2.54 cm square for analysis. The stage speed was 49.8 microns/second with a travel distance of 9 mm on the first cycle and 11 mm on the second cycle. A second cycle was run to detect any changes in the surface due to being washed in water on the first cycle. The advancing and receding contact angles were calculated by a routine supplied with the Cahn instrument; this uses a linear-regression for the buoyancy correction. Typical reproducibility
for contact-angle measurements on the same surface is 1 - 2 degrees. Two different surfaces are said to have significant contact angle differences when they are >3 degrees different.

**Application Data from Commercial Sources**

There are several examples of data cited from commercial applications of Dynamar FX 5911X in PP film. Most of these commercial processes are considered proprietary. The experimental set up for the die build-up shown in Photos 3 & 4 can be found in the publication cited as Reference 3.

**Results and Discussion**

**Examples of Application Benefits for Dynamar FX 5911X in PP Film**

Die build-up or die drool is a common problem in the manufacture of PP film and extruded articles. Polypropylene will chain scission during oxidative degradation allowing for oxidized, low MW material to adhere to the inside of the die wall. Moderate to high loading of pigments and other additives like stearates are also likely to increase die build-up frequency. The material that builds up inside the die will eventually be pushed out onto the lip where it can cause web breakage, hole formation and poor film quality through intermittent sloughing. Internal die deposits can carbonize and harden resulting in gauge variation or die lines.

Using low levels of Dynamar FX 5911X (500 ppm or less) can reduce the frequency of die build-up, extend the time between die cleanings and screen pack changes and reduce the time required for cleaning. A PP formulation containing 18% talc was run on a cast film line and demonstrated build-up in less than 1 hour. Addition of PPA eliminated the build-up out to 2 hours as shown in photos 3 & 4. Photos 5 & 6 show the result of extruding just one barrel of a moderately loaded (3%) TiO₂ containing, BOPP type formulation through a capillary die. When there is no PPA added, die build-up of pigment particles is evident. Adding 300 ppm of Dynamar FX 5911X eliminates this build-up.

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Photos 3 & 4: Cast PP film with 18% talc showing die build-up after 1 hour of extrusion with no PPA (left). The same formulation with 300 ppm of PPA shows no die build-up after 2 hours of extrusion (right).

Photos 5 & 6: Polypropylene with 3% of TiO₂ results in die build-up during capillary extrusion. Addition of 300 ppm of FX 5911X eliminates the build-up for the same amount and time of extrusion.
Another important benefit, attributable to the use of PPA, is improved film thickness or gauge control. Several theories have been offered on how a PPA can provide this benefit. The PPA causes slip at the polymer melt/extruder interface inducing plug flow in contrast to the shear flow found when high molecular weight polyethylene is extruded without a PPA. Plug flow may allow the polymer to fill and exit the die in a more consistent manner. Less die swell will also occur with the use of a PPA, allowing film thickness to be evenly controlled by take-off equipment. Flow channels and die lines can be caused by the carbonization of low molecular weight species inside the die. The PPA coating is thermally stable and prevents or removes these deposits. An example of improved gauge control is shown in the histogram comparison of film thickness, with and without FX 5911X, for a commercial cast, mono-oriented (raffia) film process (Figure 1).

Surface properties of pigmented and non-pigmented films are shown in Table 1. For the non-pigmented samples no differences are seen for coefficient of friction (CoF) properties. These formulations did not contain slip agent or antiblock so the CoF is characteristically high. Film samples were adhesive coated after corona treatment (and then after aging) and peel tests were done to measure the coating distribution and maintenance. Again, no differences were seen for PPA-containing samples compared to a control. Seal initiation temperatures were measured on the two non-pigmented films and they are also the same and within the range expected for BOPP of this type. There might be slight improvements in haze and clarity properties for the PPA. This is probably due to the smoothening of the film surface due to PPA.

Physical properties of pigmented (3% CaCO3) BOPP films, with and without 300 ppm of FX 5911X, are compared in Table 1. No significant differences are seen for elongation, tensile, modulus or shrinkage properties. The gloss for the pigmented sample containing a PPA was increased significantly. The presence of a PPA can significantly improve the surface smoothness of films and other extruded articles. Magnified BOPP film surfaces (aluminized, no pigment) show the improved smoothness for PPA containing film (Photos 7 & 8). Surface smoothness (see Photos 7 & 8) can also help reduce problems due to water carry-over in raffia and other water quenched film processes.

![Histograms comparing film gauge for mono-oriented PP (raffia) films, with and without Dynamar PPA FX 5911X](image)

Figure 1: Histograms comparing film gauge for mono-oriented PP (raffia) films, with and without Dynamar PPA FX 5911X
Table 1:
Physical Properties of Pigmented (CaCO$_3$) and non-pigmented BOPP Rims with and without Dynamar FX5911X

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>No PPA</th>
<th>PPA</th>
<th>No PPA</th>
<th>PPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (microns)</td>
<td>28.0</td>
<td>28.0</td>
<td>36.8</td>
<td>36.8</td>
</tr>
<tr>
<td>Elongation MD (%)</td>
<td>122</td>
<td>131</td>
<td>106</td>
<td>104</td>
</tr>
<tr>
<td>Elongation TD (%)</td>
<td>45</td>
<td>48</td>
<td>37</td>
<td>41</td>
</tr>
<tr>
<td>Tensile Strength @ Break MD (Kg/cm$^2$)</td>
<td>1729</td>
<td>1926</td>
<td>1376</td>
<td>1382</td>
</tr>
<tr>
<td>Tensile Strength @ Break TD (Kg/cm$^2$)</td>
<td>2637</td>
<td>2665</td>
<td>2152</td>
<td>2065</td>
</tr>
<tr>
<td>Tensile Strength @ Yield MD (Kg/cm$^2$)</td>
<td>380</td>
<td>415</td>
<td>316</td>
<td>316</td>
</tr>
<tr>
<td>Tensile Strength @ Yield TD (Kg/cm$^2$)</td>
<td>534</td>
<td>485</td>
<td>359</td>
<td>337</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td>2170</td>
<td>2212</td>
<td>2590</td>
<td>2674</td>
</tr>
<tr>
<td>Shrinkage MD (%)</td>
<td>12</td>
<td>10</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Shrinkage TD (%)</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>2</td>
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<tr>
<td>Haze (%)</td>
<td>0.52</td>
<td>0.57</td>
<td>NA</td>
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<tr>
<td>Clarity (%)</td>
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<td>98.2</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Gloss (%)</td>
<td>NA</td>
<td>NA</td>
<td>64</td>
<td>72</td>
</tr>
<tr>
<td>Opacity (%)</td>
<td>NA</td>
<td>NA</td>
<td>85.9</td>
<td>86.5</td>
</tr>
<tr>
<td>Coefficient of Friction (no slip agent)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Adhesive Peel Test (after corona)$^*$</td>
<td>Excellent</td>
<td>Excellent</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Adhesive Peel Test (after corona, aging)$^*$</td>
<td>Excellent</td>
<td>Excellent</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Seal Initiation Temperature (°C)</td>
<td>108</td>
<td>108</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

$^*$ Adhesion test is proprietary to 3M Company

Photos 7 & 8: Aluminized PP films magnified by 300X show the difference in surface smoothness for no PPAs (left) and the same formulation containing 300 ppm of FX 5911X.
During the commercial trial to produce the CaCO₃-containing BOPP films for physical properties, the die pressure was significantly reduced. Increasing the extruder RPM, to return to this initial pressure level, allowed the process to increase output by approximately 30%. Similar benefits have been seen in other commercial PP processes. Output increases of between 10 to 35% have been achieved.

**Surface Composition and Surface Polarity Measurements**

Contact angle measurements are an effective way of estimating surface energies and changes in surface energy. Polypropylene has a low surface energy and requires corona treatment to oxidize the surface to allow for printing and coating. Changes to the surface energy, making it harder to corona treat or making the oxidized surface less stable after treatment, could greatly affect the productivity of a plant making printed wrap or adhesive coated tape.

Film samples were prepared on a lab-scale Bruekner BOPP line including a control (no PPA) and 2000 ppm of FX 5911X. The high concentration of a PPA was selected in order to test the worst case scenario for PPAs existing on the surface. The films were tested periodically to determine advancing and receding contact angles as functions of aging time. Advancing contact angle measures the initial surface energy of the substrate. Receding contact angle measures the effect the liquid has on the surface. A lower receding contact angle is common because the liquid usually does affect the substrate. The results of these evaluations are shown in Figures 2 and 3, with no corresponding differences between control and PPA-containing samples. The values for receding contact angles for both film samples were lower at the 48 day aging time compared with the other results. It is not clear why these values were lower; however, the observed decreases were similar for both samples.

Film samples were also tested periodically following corona treatment to determine advancing and receding contact angles as functions of aging time after treatment. All of the samples for the above tests were stored at room temperature (approximately 20°C (68°F)) and at approximately 35% Relative Humidity (RH). The results of these evaluations are shown in Figures 4 and 5 (The contact angle values for untreated films are included in the figures as a reference). Again, no significant differences are seen for the contact angles of the control film as compared with the PPA-containing sample. A treated film roll was aged for 10 days at 50°C (122°F) and 80% RH to simulate extreme storage conditions. This sample was also tested to determine advancing and receding contact angles as functions of extreme storage conditions. The results of these tests are shown in Figures 6 and 7. Once again there is no significant difference between films with and without the PPA additive.

The results shown in Figures 4, 5, 6 and 7 indicate that for both the control film and the additive containing film, there are slight increases in advancing and receding contact angles as a function of aging time. Small decreases in wet-ability observed during aging are attributed to the reorientation of oxidized functionalities within the treated-surface region. There were no differences observed in the aging characteristics of the two films.

**ESCA Analysis**

Elemental analysis was done to look primarily for fluorine on the surface of the films. Assuming there is no contamination, fluorine should be present in the films only from a PPA. The level of a PPA added to the films was 2 to 5 times higher than the concentration normally used to derive benefits. The elemental analysis shows mostly carbon on the surface of the films. The carbon levels are not plotted in the following figures because the scale on the y-axis would be too large to show the <1% level of O, F, and Si. Silicon is a common contaminant and is measured to show the background level of noise in the measurement.

Figure 8 shows a small amount of fluorine present for both the control and PPA-containing films. The nominal level of fluorine that would be present at the surface for a 2000 ppm concentration of fluoropolymer is 1400 ppm. The level present in the control, which is most likely the background noise level for measuring fluorine, is 2000 ppm. Given this sensitivity, the differences between control and PPA films are not significant and certainly within the error normally associated with ESCA measurements. Figure 9 shows the levels after corona treatment. The oxygen level is characteristically high. No fluorine is detected for either the control or the PPA containing film. Finally, Figure 10 shows ESCA data after 10 days aging at room temperature under normal laboratory conditions. The corona treated sample shows a small amount of fluorine but at a level that is essentially the same as the control. Because the control did not originally contain any PPA, it is likely that the fluorine content of these surfaces is due to adventitious contamination of the surface rather than surface segregation. Most importantly the small amount of fluorine detected in these measurements does not at all effect wetability.

**SSIMS Analysis**

The SSIMS data again show no differences between the PPA-containing sample and a control without PPA. A small peak was seen at 19 amu (corresponding to F⁻ ion), in both spectra, but the magnitude is the same or basically a background signal. The spectra are not shown in the paper in order to save space for other data. They are available upon request.
Conclusions
Application of fluoropolymer processing additives in polypropylene is a new and exciting area for a technology that has been effective for years in polyethylene. A concerted PPA product development by Dyneon has led to new products that can provide significant benefits for polypropylene extrusion processes. These benefits include reduced die build-up, improved gauge control, faster pigment transition time, reduced gel formation, reduced process temperatures to maintain molecular weight and reduced downtime for maintenance.

There are always concerns about the effect of a surface-active additive on other properties such as printing and sealing. Knowledge of the PPA mechanism can lead to a fundamental understanding of why a PPA will not be present in sufficient quantity to alter the surface properties. To support this hypothesis, analysis of film surfaces for polarity (contact angle) and atomic fluorine show no differences for PPA-containing films compared to controls without the additive. The same is true after corona treatment and aging. Additionally there are no differences in critical physical properties such as tensile strength, modulus, tear strength and elongation. The gloss, clarity and surface smoothness of a PPA-treated extrusion article tends to be improved. This can add additional benefits such as better pigment color presentation and less water carry-over. To summarize, a polymer processing additive can provide many benefits that can improve productivity and quality without an impact on critical physical properties.

References
1. CA. Rudin, A. Worm and J. Blacklock, *J. Plast. Film Sheet*, “Fluorocarbon Elastomer Processing Aid in Film Extrusion of LLDPE’s” 1(3): 189[1985].
Figure 2: Advancing Contact Angle Measurement on Polypropylene Films With and Without PPAs

Figure 3: Receding Contact Angle Measurement on Polypropylene Films With and Without PPAs
Figure 4: Advancing Contact Angle Measurement on Polypropylene Films With and Without PPA, After Corona Treatment

Figure 5: Receding Contact Angle Measurement on Polypropylene Films With and Without PPA, After Corona Treatment
Figure 6: Advancing Contact Angle Measurement on Polypropylene Films With and Without PPA, After Corona Treatment and Aging After 10 days (50°C/80% RH)

Figure 7: Receding Contact Angle Measurement on Polypropylene Films With and Without PPA, After Corona Treatment and Aging After 10 days (50°C/80% RH)
Figure 8: ESCA Analysis of PP Films After Extrusion

Figure 9: ESCA Analysis of PP Films After Corona Treatment
Figure 10: ESCA Analysis of PP Films After Corona Treatment and Aging for 10 days (50C/80% RH)
Technical Information and Test Data

Technical information, test data, and advice provided by Dyneon personnel are based on information and tests we believe are reliable and are intended for persons with knowledge and technical skills sufficient to analyze test types and conditions, and to handle and use raw polymers and related compounding ingredients. No license under any Dyneon or third party intellectual rights is granted or implied by virtue of this information.

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